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Neutral bimetallic rhenium(I)-containing halogen and hydrogen bonding acyclic receptors for anion recognition

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ABSTRACT

Neutral bimetallic rhenium(I) bis-triazole pyrimidine halogen bonding (XB) and hydrogen bonding (HB) acyclic anion receptors are prepared and ^{1}H NMR titration investigations reveal the XB receptor exhibits significantly superior anion recognition behaviour.

Introduction

Anions are ubiquitous in nature and play numerous fundamental roles in a variety of biological, medical and environmental processes [1]. During the past few decades this has stimulated the construction of a plethora of anion receptor systems that function in polar organic and aqueous media by exploiting electrostatics, hydrogen bonding (HB), Lewis acid-base and anion-pi interactions [2]. In spite of the highly directional character and comparable bond strength to HB, the application of halogen bonding [3] (XB) for the recognition of anions has only recently begun to be investigated [4]. Importantly, the relatively few examples of XB anion receptors reported to date all exhibit contrasting anion recognition properties compared to HB analogues [2a,5].

Herein we report the synthesis and anion binding properties of a new class of neutral, bimetallic bis-triazole [6] pyrimidine based halogen bonding (XB) and hydrogen bonding (HB) acyclic anion receptor (Fig. 1). The chelation of two rhenium(I) metal centres produces highly preorganised receptors capable of strong anion binding in competitive solvent media, with the XB receptor displaying significantly enhanced levels of anion recognition with a particular affinity for iodide.

Synthesis

The target bimetallic receptor systems were synthesised *via* the initial preparation of bis-iodo- and bis-prototriazole ligands using CuAAC 'click' chemistry [7,10a,10b] and the reactant 4,6-diethynylpyrimidine. This afforded tetra-dentate ligands capable of coordinating to two rhenium (I) metal centres to produce neutral bimetallic bis-triazole pyrimidine based XB/HB receptors.

Scheme 1 outlines the synthetic routes undertaken to produce the ligands **5** and **6**. 4,6-Di-iodo pyrimidine [8] was reacted with two equivalents of TMS-acetylene under Sonogashira conditions [9] to produce TMS-protected alkyne **2** in 94% yield. Subsequent deprotection using K_2CO_3 in 1:1 ^{t}BuOH:H_2O afforded 4,6-diethynylpyrimidine **3** in 63% yield. Receptor precursor **5** was synthesised in 75% yield *via* reaction of **3** with two equivalents of octyl azide **4** [5d] in the presence of $Cu(ClO_4)_2 \bullet 6H_2O$, NaI, DBU and TBTA [10]. Precursor **6** was synthesised by *in situ* deprotection and click reaction: two equivalents of **4** and TMS-protected alkyne **2** were stirred together in a 1:1 ^{t}BuOH:H_2O solvent mixture with K_2CO_3,

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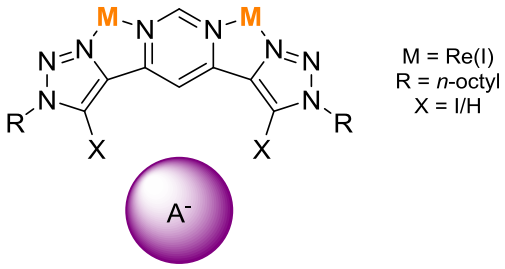
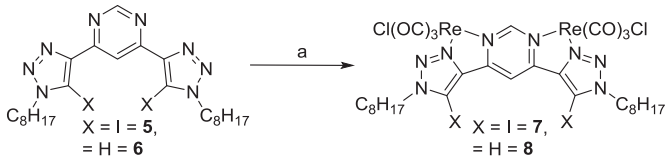


Fig. 1. Preorganised bimetallic bis-triazole pyrimidine based XB/HB receptors.



Scheme 2. Complexation of Re(I) to form anion receptors **7** and **8**. a) 2 eq. $Re(CO)_5Cl$, THF:Toluene, 100 °C, 2 h.

$CuSO_4 \bullet 5H_2O$ and (+)-sodium L-ascorbate to afford the ligand **6** in 60% yield.

Complexation reactions with two equivalents of $[Re(CO)_5Cl]$ or $[Re(CO)_3(MeCN)_2Cl]$ [11] produced the bimetallic anion receptors **7** and **8** in 75% and 25% yields respectively (Scheme 2). The receptors were characterised by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, IR spectroscopy and UV–vis absorption and luminescence emission spectroscopy (see Supporting Information).

^1H NMR spectroscopy anion binding studies

Initial ^1H NMR anion binding studies were undertaken in $CDCl_3$ with **8** and TBACl. Large downfield shifts in the resonances of the triazole H_c and *5*-pyrimidine H_b protons of the receptor (2.55 and 1.13 ppm respectively) and upfield shifting (0.21 ppm) of the *2*-pyrimidine H_a proton were taken as evidence that the halide guest was binding in the receptor cleft between the triazole protons. The changes in chemical shift of pyrimidine proton H_b were monitored and a 1:1 stoichiometric association constant of $K_a > 10^4$ M^{-1} determined by Job plot and WinEQNMR2 analysis [12].

With evidence of strong chloride binding in chloroform, a more competitive protic solvent mixture of 1:1 $CDCl_3$:CD_3OD was selected in order to elucidate the anion binding properties of **7** and **8** receptors using analogous ^1H NMR titration experiments with a variety of anions (Fig. 2).

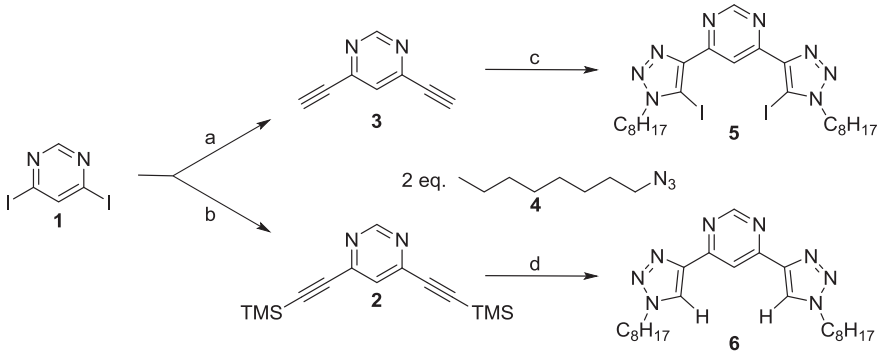
With the exception of perchlorate and XB receptor **7,** the addition of halides and a range of oxoanions caused significant perturbations of the respective receptor's ^1H NMR spectrum, namely downfield shifts of pyrimidine proton H_b and the triazole protons in the case of **8,** concomitant with upfield shifting of pyrimidine proton H_a. For example, Fig. 3 displays the titration binding isotherms of receptor **7** with halides, highlighting iodide recognition produces the largest downfield shift of pyrimidine proton H_b (0.62 ppm). Fig. 4 shows the titration binding isotherms of receptor **8** with oxoanions. WinEQNMR2 [12] analysis of the titration data monitoring pyrimidine H_b or triazole H_c determined 1:1 stoichiometric anion association constants shown in Table 1.

Importantly, XB receptor **7** exhibits in general superior anion binding affinity and degree of selectivity over HB receptor **8**. For example amongst the halides, whereas HB receptor **8** displays a modest selectivity for chloride, XB receptor **7** exhibits very strong binding of all the halides and selectivity for iodide. Contrasting strength of binding and selectivity trends are also observed with oxoanion guest species. The XB receptor binds hydrogen carbonate strongly in preference to nitrate followed by acetate and dihydrogen phosphate, and does not bind perchlorate. By contrast the HB receptor is selective for nitrate over dihydrogen phosphate > perchlorate > hydrogen carbonate and binds acetate weakly. By virtue of increased negative charge, sulfate forms strong associations with both receptors, with HB receptor being the more potent host. We have recently demonstrated a significant covalent contribution [5d] to halogen bonding-anion recognition in acyclic and catenane XB receptors. The combination of this covalent contribution with the stringent directionality of XB donor motifs together with steric effects are likely to dictate the experimentally observed contrasting anion binding affinities and selectivity trends of XB receptor **7** with the HB receptor analogue **8**.

Preliminary UV–Vis and luminescence studies

Rhenium (I) complexes that contain triazole ligands exhibit well documented photophysical properties [13]. It was anticipated that the bimetallic receptors would have the capability of sensing anions *via* optical means. The photophysical properties of receptors **7** and **8** are displayed in Table 2.

Qualitative UV–Vis absorption spectroscopy anion titration experiments in acetonitrile revealed notable changes in the wavelength maxima and absorptivity of the receptors' electronic spectra (Fig. 5). For example, XB receptor **7** exhibited hypsochromic shifting of the lowest energy MLCT band at $\lambda = 430$ nm (19 nm), concomitant with an increase in absorptivity ($\varepsilon = 9500$ M^{-1} CM^{-1}), in the



Scheme 1. Synthesis of receptor precursors **5** and **6**. a) (i) 2.5 eq. TMS-acetylene, $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N, THF, 85 °C, 48 h (ii) 2.2 eq. K_2CO_3, ^tBuOH:H_2O, 1 h (63%); b) 2.5 eq. TMS-acetylene, $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N, THF, 85 °C, 48 h (94%); c) 2.5 eq. 4, $Cu(ClO_4)_2 \bullet 6H_2O$, NaI, TBTA, DBU, THF, RT, 24 h (75%); d) 2.5 eq. 4, K_2CO_3, $Cu(SO_4)_2 \bullet 5H_2O$, (+)-sodium L-ascorbate, ^tBuOH:H_2O (60%).

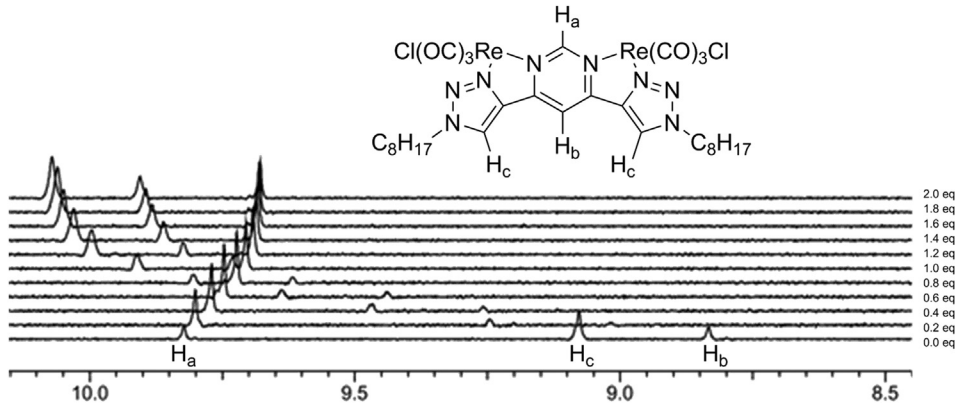


Fig. 2. 1H NMR spectral changes observed in **8** in 1:1 $CDCl_3$:CD_3OD upon addition of up to two equivalents of sulfate ions. Only relevant aromatic signals are visible in the spectral range displayed (T = 298 K).

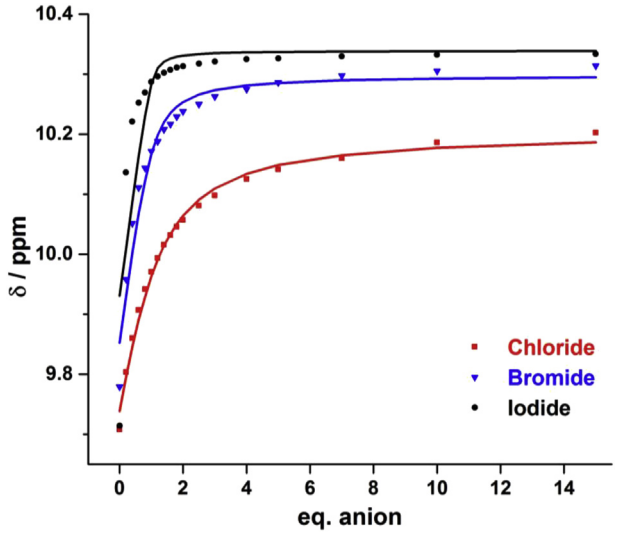


Fig. 3. Experimental titration data (points) for H_b and the fitted binding isotherm (lines) recorded in 1:1 CD_3OD:$CDCl_3$ at 298 K and 500 MHz for XB receptor **7** upon addition of halide anions.

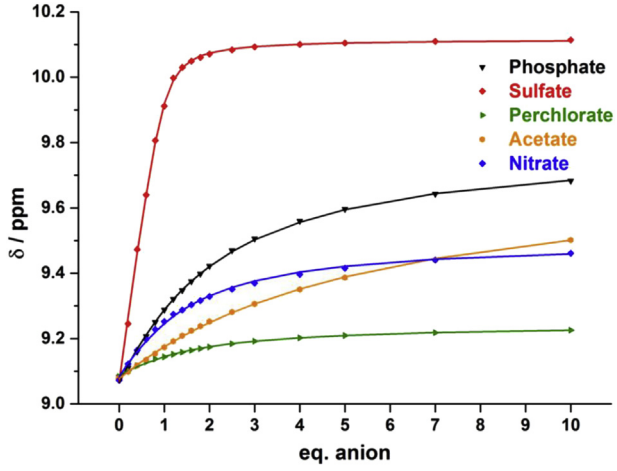


Fig. 4. Experimental titration data (points) for H_c and the fitted binding isotherm (lines) recorded in 1:1 CD_3OD:$CDCl_3$ at 298 K and 500 MHz for HB receptor **8** upon addition of oxoanions.

presence of sulfate ions and similar spectral perturbations were observed with the range of anions studied (see supplementary information).

Excitation at $\lambda_{ex} = 450$ nm of an acetonitrile [14] solution of each receptor produced the expected ^{3}MLCT emission as a broad band at $\lambda_{em} = 519$ nm ($c = 2 \times 10^{-5}$ M, T = 298 K) for both systems, which is in agreement with similar rhenium(I) triazole containing complexes previously reported [2a,13b,c]. The addition of sulfate, dihydrogen phosphate and halide anions all caused in general an increase in the ^{3}MLCT emission band intensity for both XB and HB receptors **7** and **8** (see supplementary figures). This may be a consequence of anion binding by the receptors causing an increased rigidification of the host system which disfavours non-radiative decay pathways [15].

Preliminary modelling studies

To shed some light into the binding affinity of **7** towards the halide series, DFT calculations were undertaken on model complexes with Gaussian 09 [16] at the M06-2X level of density functional [17]. The rhenium centres were described with the LANL2TZ(f) [18] basis set with effective core potentials while for the chlorine atoms the aug-cc-pVTZ [19] basis set was applied. The larger halogen atoms were treated with the aug-cc-pVTZ-PP basis set [20] and the remaining elements were described using the 6-311++G(d,p) basis set [21].

A model ligand $\mathbf{7_{methyl}}$, incorporating the central XB binding motif of **7** and methyl groups replacing the longer *n*-octyl substituents, was built by atomic manipulation of a suitable crystal structure. This rigid model of **7** was initially optimised in gas phase considering two geometric isomers: The three carbonyl groups are distributed around each octahedral rhenium in *fac* positions, but with the two chlorine atoms adopting a *cis* or a *trans* spatial disposition. The *trans* isomer, shown in Fig. 6 (left), is slightly favoured by 1.84 kcal mol^{-1} and was then used in the subsequent DFT calculations of the halide complexes. Moreover, the distribution of the electrostatic potential mapped onto the electron density surface of *trans* geometric isomer was also calculated and is presented in Fig. 6 (middle and right). $\mathbf{7_{methyl}}$ has a well-defined positive surface enclosing the XB binding region (red area) with two maxima of 60.9 kcal mol^{-1}, one in front of each iodine atom, illustrated with the black dots in Fig. 6. On the other hand, the most negative regions of the electrostatic potential (blue areas) surround the $Re(CO)_3Cl$ fragments of $\mathbf{7_{methyl}}$.

The DFT optimised structures of the halide complexes are also shown in Fig. 7. The XB dimensions, gathered in Table 3, show that

Table 1
Anion association constants (M^{-1}) for Rhenium(I) receptors **7** and **8** in 1:1 $CDCl_3$:CD_3OD[a] at 298 K.

Anion[b]	Cl^-	Br^-	I^-	HCO_3^-	AcO^-	$H_2PO_4^-$	ClO_4^-	SO_4^{2-}	NO_3^-
7 (XB)	883 (102)	4070 (158)	>**10**^{4c}	1904 (75)	218 (18)	123 (44)	n.b.[d]	8×10^{3c}	424 (6)
8 (HB)	409 (41)	168 (9)	338 (20)	226 (3)	92 (3)	302 (10)	430 (21)	$>10^{4c}$	548 (32)

[a] Recorded at 500 MHz.
[b] Anions added as their tetrabutylammonium salts, except HCO_3^- which was added as a tetraethylammonium salt.
[c] Binding too strong to accurately determine *via* WinEQNMR2 analysis.
[d] n.b. no binding; no change in ^{1}H NMR spectrum was observed upon addition of anion. Values in parentheses are calculated errors, experimental errors <10%.

Table 2
Photophysical properties of bimetallic anion receptors **7** and **8** in acetonitrile at 298 K.

	λ_{abs}[a]	Assignment [13b,c]	ε[b]	λ_{em}[a,c]
7 (XB)	329	MLCT	12,890	
	430	MLCT	7180	519
8 (HB)	244	IL/LLCT	22,600	
	310	MLCT	24,050	
	422	MLCT	10,840	519

[a] nm.
[b] M^{-1} cm^{-1}.
[c] Following excitation at λ_{ex} = 450 nm.

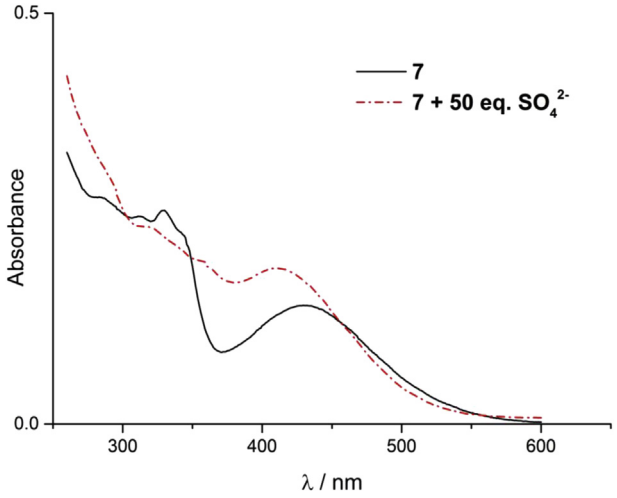


Fig. 5. UV–Vis absorption spectral changes observed addition of sulfate to **7** (acetonitrile, $c = 2 \times 10^{-5}$ M, T = 298 K, λ_{ex} = 450 nm).

the central core of **7** establishes with each halide two cooperative and almost linear XB interactions with equal dimensions. In agreement with the existence of XB interactions, the optimised distances between the iodine and halide anions ($I\cdots X^-$, with $X^- = Cl^-$, Br^- or I^-) are shorter than the sum of the iodine van der Waals radius and the halide ionic radius. However, it is noteworthy that the difference between these two values increases in the order Cl^- (0.09 Å), Br^- (0.18 Å) and I^- (0.21 Å). Furthermore, concomitantly with the increasing of $I\cdots X^-$ distances, the $C{-}I\cdots X^-$ angles show a slight increase towards the linearity (180°), along the halide series from Cl^- to I^-. This structural comparison suggests the XB interactions are stronger in complexes with larger anions, namely with iodide. The strength of XB interactions was further ascertained through the calculation of the Wiberg bond index [22]. The Wiberg bond indices are 0.151, 0.167, and 0.178 for the Cl^-, Br^- and I^- complexes, respectively, which indicate that in the iodide complex, the two XB interactions have a higher covalence character than in the remaining two halide complexes.

In summary, our preliminary theoretical study shows that the XB interactions are stronger in the iodide complex of $\mathbf{7}_{\mathbf{methyl}}$, in agreement with the experimental binding affinity trend found for **7** in the solvent mixture 1:1 MeOD:$CDCl_3$.

Conclusions

In summary, neutral bimetallic rhenium(I) bis-triazole pyrimidine halogen bonding (XB) and hydrogen bonding (HB) acyclic anion receptors were prepared and shown by ^{1}H NMR anion titration experiments to bind a range of anions in a competitive protic solvent medium. Importantly, the XB receptor was demonstrated to be a significantly superior anion recognition host displaying notable selectivity for halides, in particular for iodide, over a variety of monocharged oxoanions. The incorporation of this new bimetallic XB donor motif into cyclic and interlocked host structural frameworks for anion recognition and sensing purposes is continuing in our laboratories.

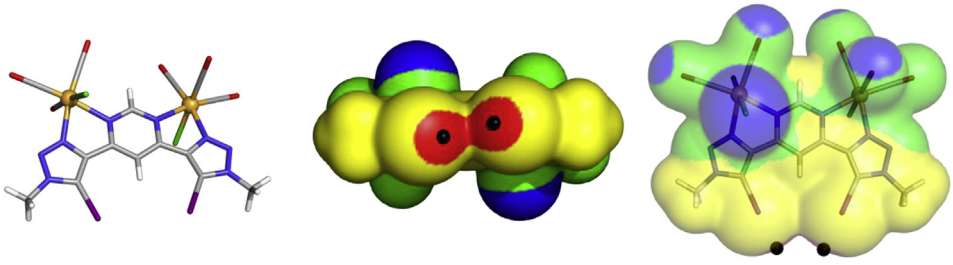


Fig. 6. DFT optimised structure of model ligand $\mathbf{7}_{\mathbf{methyl}}$ (left) together with the corresponding distribution of the electrostatic potential onto the electron density surface: middle – binding units view point; right – top view point, with transparency. $\mathbf{7}_{\mathbf{methyl}}$ is shown in sticks, with the hydrogen atoms shown in white, the carbon atoms in grey, the nitrogen atoms in blue, the oxygen atoms in red, the chlorine atoms in green, the iodine atoms in purple and the rhenium atoms in orange. Colour ranges, in kcal mol^{-1}, are blue, lower than −23.0; green, from −23.0 to 10.5; yellow, from 10.5 to 44; red higher than 44. The most positive values, $V_{S,max}$, are identified by black dots (60.9 kcal mol^{-1}), and correspond to the σ-holes on the iodine bis-triazole substituents. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

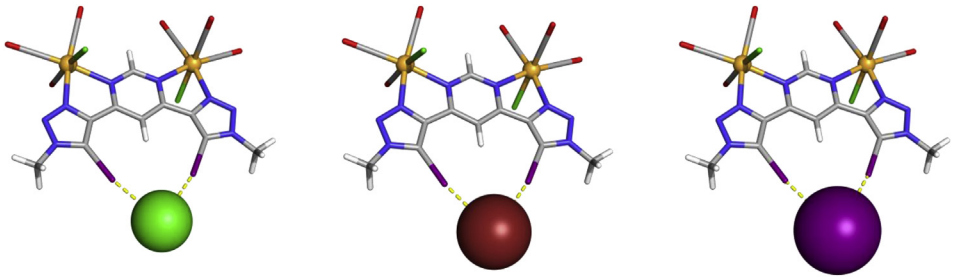


Fig. 7. DFT optimised structures of $\mathbf{7}_{\mathbf{methyl}}$ XB complexes with chloride (left), bromide (middle) and iodide (right). The XB interactions are drawn as yellow dashed lines. The halides are shown as green, brown and purple spheres for chloride, bromide and iodide, respectively. Remaining colouring details as given in Fig. 6. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
XB dimensions in $\mathbf{7}_{\mathbf{methyl}}$ halide complexes.

X	C–I distance (Å)	I···X$^-$ distance (Å)	C–I···X$^-$ angle (°)
Cl$^-$	2.106; 2.106	2.955; 2.955	167.8; 167.8
Br$^-$	2.109; 2.109	3.107; 3.107	169.1; 169.1
I$^-$	2.109; 2.109	3.317; 3.317	170.5; 170.5

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.04.039.

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